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Phase-transfer catalysis applied to the oxidation of nonaqueous phase trichloroethylene by potassium permanganate

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Abstract

The use of potassium permanganate to oxidize chlorinated solvents has been demonstrated as an effective process for treating nonaqueous phase liquids in ground-water systems. This study evaluates the effectiveness of phase-transfer catalysts (PTCs) in enhancing the degradation rate. PTCs work by transferring permanganate ion into the nonaqueous phase where it initiates oxidative decomposition. We studied the oxidation of trichloroethylene (TCE) by potassium permanganate, conducting kinetic batch experiments in conjunction with three PTCs that varied in terms of their extraction constants and molecular structures. Using the same batch technique, we examined whether PTCs could enhance the aqueous solubility of TCE. Solubilization could also increase oxidation rates in the aqueous phase. Rates of TCE oxidation in solutions containing the PTCs and a blank were estimated separately by measuring chloride concentration and UV–Vis absorbance in the aqueous phase. The enhanced rate of TCE destruction by the PTCs was reflected by an increase in the rate of consumption of permanganate ion and production of chloride ion. There was no tendency for the PTCs, however, to solubilize TCE in the aqueous phase. Therefore, the PTCs increased the rate of TCE decomposition by catalyzing permanganate oxidation in the organic phase. This study suggests that there is significant potential for testing this scheme under field conditions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Phase-transfer catalyst; Potassium permanganate; Trichloroethylene; Nonaqueous phase; Remediation

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1. Introduction

Chlorinated ethylenes such as trichloroethylene (TCE) and perchloroethylene (PCE) are common contaminants (Westrick et al., 1984; Plumb, 1991). They occur in the subsurface as zones of residual saturation or occasionally as free products. Because of their inherently low solubility, dense nonaqueous phase liquids (DNAPLs) persist in aquifers and provide a long-term source of dissolved contaminants, capable of being transported (Johnson and Pankow, 1992).

Given the difficulties in remediating DNAPL contaminated sites, there has been a lot of effort to develop and to demonstrate new technologies. Our focus here is on oxidative schemes. In particular, oxidative decomposition with potassium permanganate (Schnarr et al., 1998; Yan, 1998; Yan and Schwartz, 1999) or hydrogen peroxide (Glaze and Kang, 1988) has been demonstrated as an effective process for mineralizing chlorinated solvents in the aqueous phase. Unlike reductive dechlorination, the oxidation of chlorinated solvents does not produce hazardous intermediates, such as dichloroethylene and vinyl chloride (Vella and Veronda, 1992; Vogel et al., 1987).

Potassium permanganate ($KMnO_4$) has been widely examined for the oxidative dechlorination of TCE in bench scale or pilot scale experiments (Vella and Veronda, 1992; Yan, 1998; Yan and Schwartz, 1999). A recent study on the permanganate dechlorination of TCE has documented reaction mechanisms and pathways, and has identified main intermediate products at different pHs (Yan, 1998). Our group has completed a model capable of simulating permanganate oxidation under field situations (Zhang and Schwartz, 2000).

Both laboratory and modeling results pointed out how constraints on the solubility of chlorinated solvents in the aqueous phase ultimately control the rate of oxidative destruction. Permanganate oxidation occurs only in the aqueous phase and involves dissolved species such as permanganate ion (MnO_4^-) and the chlorinated ethylenes. Thus, the solubility of the contaminants indirectly controls the utilization of MnO_4^- in the reaction and keeps the reaction rate relatively small.

Our efforts to increase the permanganate oxidation rate were initially concentrated on methods to enhance the solubility of chlorinated ethylenes in the aqueous phase. We first tried to exploit cosolvency effects, utilizing various alcohol–water mixtures to increase TCE solubilization and ultimately, the rate of oxidation. However, non-ideal behavior of MnO_4^- in the cosolvent phase, as yet poorly understood, and competition between the cosolvent and the target contaminant for MnO_4^- frustrated this approach.

This paper outlines a new concept, which is based on phase-transfer catalysis, to accelerate the oxidation of chlorinated solvents. Phase-transfer catalysis attempts to speed up the overall rate of DNAPL oxidation by enabling the oxidation to occur in both the aqueous and DNAPL phases. In a conventional oxidation scheme with two immiscible phases in contact (water and DNAPL), the oxidation of chlorinated compounds only occurs in the aqueous phase because that is where the MnO_4^- is present. Adding a phase-transfer catalyst (PTC) transfers some of MnO_4^- to the nonaqueous phase. Thus, MnO_4^- can oxidize chlorinated compounds both in the aqueous phase and in the pure-phase solvent.

The specific objectives of this study are to introduce the concept of phase-transfer catalysis for the oxidation of chlorinated solvents and to evaluate whether the catalyzed oxidation scheme can enhance the oxidation of TCE with MnO_4^-. We conducted kinetic batch experiments to verify the hypothesis that PTCs would promote the oxidation of TCE in the nonaqueous phase and speed up the overall rate of TCE decomposition. We also examined whether the accelerated TCE decomposition in the presence of PTCs might be related to the enhanced solubilization of TCE in the aqueous phase by PTCs.

2. Theoretical background

Since Starks (1971) proposed a mechanistic concept for catalytic reactions occurring in the presence of two phases and catalysts, phase-transfer catalysis has become a powerful tool for developing new types of reactions and chemicals in the field of synthetic organic chemistry. Phase-transfer catalysis is a technique for converting similar chemical species situated in two or more phases. Because of its polarity, an ionic species cannot normally enter nonpolar organic substances. However, once it combines with a PTC, the organic phase can extract the association of ionic species with the PTC from the aqueous phase.
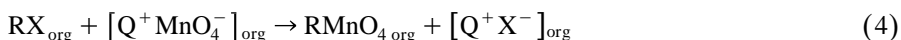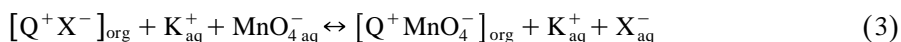
Common PTCs include organic-soluble cations such as quaternary ammonium or phosphonium ions, which contain both lipophilic and hydrophilic moieties. Due to their amphiphilic nature, the catalysts distribute themselves between aqueous and organic phases, form an association with the reactive anion (e.g. MnO_4^-), and bring them into the organic phase in a form suitable for reactions. It is presumed that PTCs would not be consumed but perform the transfer function repeatedly.

When PTCs dissolve in water, they dissociate into catalytic cations (Q^+) and counter anions (X^-), which occur as free ions like MnO_4^-. In nonpolar solvents, the associations of catalysts and ionic species exist as ion pairs (Bränström, 1977). Ion pairs are neutral entities formed by the coulombic binding of oppositely charged ions (Dehmlow and Dehmlow, 1983). An important distinction between free ions and ion pairs is that solutions containing only ion pairs are not electrically conductive. Ion pairs are thermodynamically in equilibrium with the free ions:

$$Q^+ + X^- \leftrightarrow [Q^+X^-] \tag{1}$$

where $[Q^+X^-]$ is an ion pair.

The reaction of an organic compound with MnO_4^- in the presence of PTCs (Fig. 1) can be represented by an overall equation (Eq. 2), conceptually involving two separate steps (Starks et al., 1994), a transfer step (Eq. 3) and an intrinsic displacement reaction step (Eq. 4):

$$K_{aq}^+ MnO_{4\,aq}^- + RX_{org} \overset{[Q^+X^-]}{\to} K_{aq}^+ X_{aq}^- + RMnO_{4\,org} \tag{2}$$

$$[Q^+X^-]_{org} + K_{aq}^+ + MnO_{4\,aq}^- \leftrightarrow [Q^+MnO_4^-]_{org} + K_{aq}^+ + X_{aq}^- \tag{3}$$

$$RX_{org} + [Q^+MnO_4^-]_{org} \to RMnO_{4\,org} + [Q^+X^-]_{org} \tag{4}$$

where R is the organic reactant (e.g., TCE) with a leaving group X (e.g., Cl^-). As depicted in Fig. 1, the transfer step involves the extraction of MnO_4^- from the aqueous
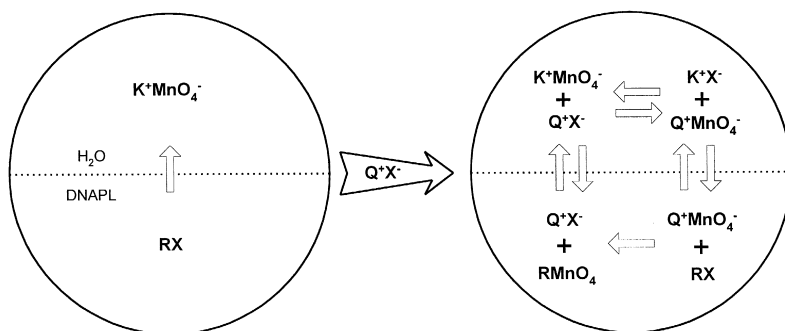
Fig. 1. Schematic diagram for PTC facilitated permanganate oxidation of TCE.

to the organic phase and the release of Cl^- back into the aqueous phase. Intrinsic displacement reaction describes the displacement of chloride ion on the target organic compound with MnO_4^-. It occurs when the transferred MnO_4^- is dissociated from the ion pair, oxidizes the chlorinated solvent, and disengages Cl^- from the organic compound.

Eq. (3) includes two simpler conversion processes (Eqs. 5 and 6) consisting of equilibria between free ions and ion pairs and transfer of ion pair into the organic phase:

$$Q^+_{aq} + MnO^-_{4\,aq} \leftrightarrow [Q^+MnO_4^-]_{org} \tag{5}$$

$$Q^+_{aq} + X^-_{aq} \leftrightarrow [Q^+X^-]_{org} \tag{6}$$

The ability of MnO_4^- to transfer into the organic phase is reflected by the relative distribution of MnO_4^- between the two separate phases. From Eq. (5), one can define the extraction constant (K_E). It represents the capability of the nonpolar solvent to extract an ionic species from the aqueous phase, and is expressed in Eq. (7). This constant is related in turn to experimentally determined solubilities (Karaman et al., 1984) by way of Eq. (8):

$$K_E = \frac{[Q^+MnO_4^-]_{org}}{[Q^+]_{aq} \cdot [MnO_4^-]_{aq}} = \frac{[Q^+MnO_4^-]_{org}}{[MnO_4^-]^2_{aq}} \tag{7}$$

$$K_E = \frac{\text{solubility of } QMnO_4 \text{ in organic solvent (M)}}{(\text{solubility of } QMnO_4 \text{ in water})^2 (M^2)} \tag{8}$$

Thus, the degree of extraction (K_E) increases in direct proportion to the solubilities of the ion pair in the organic phase.

Conceptualization of the extraction process in terms of an extraction constant can be somewhat misleading because other side processes could be important (Bränström, 1976). They impact the concentration of either the ion pairs in the organic phase or the ionic species in the aqueous phase, which subsequently can change the degree of extraction. Despite this limitation, there were reasonable agreements between the calculated extraction constants and the experimentally obtained values (Karaman et al., 1984). Therefore, a rough estimate of the extraction constants provides a useful guide in predicting the magnitude of MnO_4^- transfer.

Successful use of phase-transfer catalysis for enhancing the oxidation of TCE by MnO_4^- requires the optimal matching of organic phases and PTCs to obtain the maximum ionic transfer. For illustrative purposes, consider a case where an oxidation scheme is used to remediate a ground-water system contaminated by a single chlorinated solvent. The contaminant in this case is considered as an organic phase as well as a target organic reactant (RX_{org}). The extraction capability of the chlorinated solvent depends on the chemical structure (Bränström, 1976). Generally, somewhat more polar solvents have greater capabilities in extracting ion pairs but strongly nonpolar solvents reduce the solubility of PTCs in the organic phase to such an extent that reactions are slowed or inhibited (Table 1).

Although some organic solvents (e.g., TCE) have small extraction constants, significant extraction can be achieved by selecting an appropriate ionic reactant and PTC. Because MnO_4^- has a high affinity for association with most of the catalytic cations and the ion pair has a high lipophilicity (Makosza and Bialecka, 1976), the selection of catalysts is a key element in the design of an effective catalytic oxidation scheme. Extensive solubility measurements made by Karaman et al. (1984) reveal that the structure of the catalyst is one of the most important factors determining the efficiency of catalysis. There is a linear relationship between the solubility of the ion pair and the number of carbon atoms for quaternary ammonium with different solvents (Table 2). Quaternary cations with larger radii also have the advantage of a smaller activation energy, which facilitates the release of the ionic reactant from the ion pair and participation in the displacement reaction (Ugelstad et al., 1966; Starks, 1997). However, the use of quaternary ammonium with long alkyl groups would promote the generation of a stable emulsion that inhibits the transfer of aggregated ion pairs (Starks, 1971; Rao and Rao, 1991). The increasing activation efficiency with symmetrical quaternary cations having longer alkyl groups also levels off in the range of pentyl to octyl (Starks, 1997). Therefore, quaternary cations with extremely long alkyl chains would not be recommended in choosing a PTC.

In addition to the structure, the concentration of the catalyst is also an important factor in speeding up the catalysis reaction. Because the reaction rate is dependent on the

Table 1

Effect of selected organic solvents on extraction constants of tetrabutylammonium bromide (Bränström, 1976)

Solvent	$K_{E-NBu4Br}$
CH_3CHCl_2	0.5
$ClCH_2-CH_2Cl$	6.1
$ClCH_2-CHCl_2$	8.6
$Cl_2CH-CHCl_2$	145
C_6H_5Cl	< 0.1
$o\text{-}Cl_2C_6H_4$	< 0.1
$CH_2=CCl_2$	< 0.1
$trans\text{-}ClCH=CHCl$	< 0.1
$cis\text{-}ClCH=CHCl$	33
$ClCH=CCl_2$	0.2

Table 2
Effect of catalyst structure on solubilities (M) of quaternary ammonium and phosphonium permanganates
(Karaman et al., 1984)

Cation	CH_2Cl_2	$CHCl_3$	$C_6H_5CH_3$	CCl_4	H_2O
Tetraethylammonium	0.235	a	b	b	7.30×10^{-2}
Tetra-*n*-butylammonium	0.076	a	b	b	3.83×10^{-2}
Tetra-*n*-propylammonium	0.417	0.221	3.44×10^{-4}	2.96×10^{-5}	2.10×10^{-2}
Tetra-*n*-pentylammonium	0.482	0.261	5.59×10^{-5}	2.42×10^{-5}	9.29×10^{-5}
Tetra-*n*-hexylammonium	0.545	0.339	5.81×10^{-5}	3.51×10^{-5}	b
Tetra-*n*-heptylammonium	0.645	0.604	6.28×10^{-5}	7.48×10^{-5}	b
Tetra-*n*-octylammonium	0.713	0.229	4.02×10^{-4}	5.93×10^{-4}	b
n-Propyltriphenylphosphonium	0.083	1.03	3.57×10^{-5}	b	1.09×10^{-4}
n-Butyltriphenylphosphonium	1.16	1.15	3.18×10^{-5}	b	3.80×10^{-4}
n-Pentyltriphenylphosphonium	1.46	1.56	2.38×10^{-4}	b	2.40×10^{-4}
n-Hexyltriphenylphosphonium	1.36	1.28	2.02×10^{-4}	b	7.63×10^{-4}
n-Heptyltriphenylphosphonium	1.36	1.28	2.02×10^{-4}	b	7.53×10^{-4}

a: unstable, b: insoluble.

catalyst concentration, using a small quantity of catalyst would only make sense if the conversion is highly exothermic or the catalyst is very expensive. However, care is required in increasing the concentration of a catalyst beyond the solubility of catalyst-anion salts in the aqueous phase in order to avoid potential aggregation or precipitation of solids causing pore plugging.

Physical disturbance of the phases in the reaction system is also an important factor controlling the transfer step. Without the agitation, which is the case in ground-water systems, interfacial diffusion would be the main driving force for anion transfer. Phase transfers could be increased when tiny droplets of one phase end up scattered in the other. This distribution of phases maximizes the interfacial area for diffusional anion transfers. This effect could be important in ground-water settings. The relatively intimate dispersal of one phase in another is often found with the residual saturation of the nonwetting fluid in ground-water/DNAPL systems (Wilson and Conrad, 1984). In laboratory experiments, some agitation is essential not only to enhance the transfer but also to break down the thin stagnant layer occurring at the interface (Tomoi and Ford, 1981). With an increasing agitation rate, the overall rate of the catalytic reaction increases. Eventually, the point is reached where the intrinsic displacement process becomes rate controlling rather than the transfer step (Landini et al., 1986).

There have been many studies of the reactions between MnO_4^- and various alkenes in the organic phase (Harris and Case, 1983; Lampman and Sharpe, 1983; Ogito and Mochizuki, 1979; Sala and Sargent, 1978; Sam and Simmons, 1972; Starks, 1971; Weber and Shepherd, 1972). Due to the high reactivity of MnO_4^-, fast reactions between MnO_4^- and alkenes were reported in common solvents such as benzene and methylene chloride. Nonetheless, few experimental results are available for TCE degradation in an organic phase. Also, the lack of solubility data for common PTCs except tetra-*n*-butylammonium in TCE makes it difficult to predict MnO_4^- transfer into the pure TCE phase. As a proof-of-concept work, our study was concentrated on the enhancement of

overall TCE decomposition with permanganate oxidation in the presence of pure TCE phase and selected PTCs, instead of individual processes like MnO_4^- transfer and organic-phase displacement reactions.

3. Materials and methods

3.1. Phase-transfer catalyst

Three PTCs, tetra-*n*-ethylammonium bromide (TEA, $(C_2H_5)_4NBr$, 99.9%), tetra-*n*-butylammonium bromide (TBA, $(CH_3(CH_2)_3)_4NBr$, 99.9%), and pentyltriphenylphosphonium bromide (PTPP, $CH_3(CH_2)_4P(C_6H_5)_3Br$, 99.8%) were obtained from Aldrich Chem. The catalysts were selected on the basis of their extraction constants (K_E) and molecular structures (Table 3). Due to the lack of available solubility data for TCE, estimated extraction constants for methylene chloride were used to guide the selection of PTCs. The concentration of selected PTCs in all experiments was kept below the aqueous phase solubility in order to avoid aggregation and precipitation of catalyst-permanganate salts.

3.2. Permanganate oxidation

We conducted kinetic batch experiments to study the rate of permanganate oxidation of TCE in the presence of the selected catalysts. The $KMnO_4$ solution (2.5 mM) was prepared by dissolving $KMnO_4$ crystals in a phosphate-buffered solution (0.1 M, $KH_2PO_4:K_2HPO_4$, pH = 8). Concentrated catalyst stock solutions were also prepared with the buffer solution. Based on previous research (Makosza and Bialecka, 1976; Dehmlow and Dehmlow, 1983), it was assumed that the catalysts would hardly mobilize phosphate ion and as a result, the interference on the interaction between permanganate ion and the catalyst would be negligible. Four sets of 9-ml test tubes with Teflon-lined caps were utilized. Each set was made up of 12 tubes and the four sets were allocated to the three catalysts and one control, respectively. 3.0 ml of $KMnO_4$ solution was placed in the test tubes and 0.1 ml of concentrated catalyst solution was added to the tubes to provide a final catalyst concentration of 10 mol% $KMnO_4$. After the solution was

Table 3
Chemical properties of selected PTC–MnO_4^- ion pairs

Name/PTCs	Abbr.	FW[a]	S_w^{b}	S_o^{b}	$\log K_E^{c}$
Tetraethylammonium	TEA	165.71	7.30×10^{-4}	0.235	1.64
Tetrabutylammonium	TBA	277.92	2.10×10^{-4}	0.417	4.98
Pentyltriphenylphosphonium	PTPP	413.35	2.40×10^{-4}	1.460	7.40

FW: formula weight (g/mol); S_w: solubility (M) in water; S_o: solubility (M) in methylene chloride.
[a] Formula weight of bromide salts only.
[b] Karaman et al. (1984).
[c] Calculated with Eq. (8).

homogenized with gentle shaking, we added 1.0 ml of TCE (99.5%, Aldrich Chem.) to the permanganate solution. All of the test tubes were stirred frequently to keep the solution homogeneous but not mixed so intensely that a TCE macroemulsion formed or the surface area of the TCE changed. A 1.5-ml sample from the aqueous phase was taken from one tube of each set every 5 min. We evaluated samples for TCE degradation by measuring the chloride concentration and UV absorbance for MnO_4^-.

A 1.0-ml sample was transferred into a quartz cuvette with 1-cm pathline and scanned using a Varian Cary 1 UV–Vis spectrophotometer at wavelengths ranging from 400 to 600 nm. The phosphate buffer solution was scanned as a reference. In this range of wavelengths, MnO_4^- has a maximum absorbance at 525 nm and is almost transparent at 418 nm (Stewart, 1965). The absorbance at 418 nm is a measure of the concentration of either cyclic hypomanganate ester (Lee and Brownridge, 1973; Wiberg et al., 1973) or a soluble form of colloidal manganese dioxide (Mata-Perez and Perez-Benito, 1985; Simandi and Jaky, 1976).

The addition of PTCs to the permanganate solution did not impact the UV absorbance across the range of wavelengths of interest. UV absorbance was also used to monitor the consumption of PTCs in the permanganate reaction. UV absorbance, measured for a control without TCE, did not show any difference from the initial scan after more than 30 days.

Chloride concentration was measured using a Labconco Digital Chloridometer, which works by a coulometric titration of chloride ions (Cotlove, 1958). A 0.1-ml aliquot was mixed with 0.1 ml of sodium thiosulfate (6 mg/ml) in a 5.0-ml reaction vessel. The sodium thiosulfate acts as reducing agent to quench the oxidation reaction in the sample solution. 3.0 ml of concentrated acid reagent (0.4 N HNO_3 and 40% glacial acetic acid) was added to the reaction vessel before finally adding four drops of gelatin reagent. The samples in the reaction vessel were titrated at the HIGH switch position. The measured concentrations (mEq/l) for Cl^- in the sample were compared with those for standards. Chloride standards were prepared using KCl dissolved in the same phosphate buffer solution with the same concentration of $KMnO_4$ and catalysts. Thus, a separate set of standard was prepared for each catalyst and the control. All experiments were conducted at room temperature of $22 \pm 1°C$.

3.3. Solubility enhancement

The kinetics of TCE dissolution in the aqueous phase was measured in order to examine the influences of the catalysts on TCE solubility. The same kind of kinetic batch experiments was also employed, except that $KMnO_4$ was absent from the aqueous phase. 6.0 ml of phosphate buffer (0.1 M) was mixed with a 0.2-ml solution of concentrated catalyst in 9.0-ml test tubes, before adding a 1.0-ml of TCE. Three samples (4.0 ml) were collected from the aqueous phase at 0.5, 1, and 24 h. The sample solution was transferred into a 9.0-ml centrifuge tube and centrifuged for 10-min at 2500 rpm. The solution was diluted with deionized water (1/1000). 1.8 ml of diluted sample was mixed with 5.0 ml of pentane in 25-ml amber bottles in order to extract the organic compounds. The bottles were agitated on a platform shaker for 30 min and equilibrated for 1 h before taking samples for GC analysis. The pentane extractant was analyzed

using a Fisons Instruments 8060 gas chromatograph equipped with a Ni[63] electron capture detector and a DB-5 capillary column (J&W Scientific, Rancho Cordova, CA), 30 m × 0.32 mm I.D. with a film thickness of 1.0 μm. Helium was the carrier gas and nitrogen the make-up gas. For calibration standards, TCE in methanol was mixed with phosphate buffer solution containing catalysts. We kept the volume of methanol added small (0.1% of total volume) in order to minimize cosolvent effects. For consistency, the same procedures were followed in preparing the standards for consistency. Separate standards were prepared for each catalyst and the control.

4. Results and discussion

4.1. Chloride concentration measurements

Because of the pure TCE phase in the system, it was not feasible to monitor TCE loss with time as a measure of oxidation rate. However, the time variation in the concentration of chloride ion can serve as an indicator for the TCE breakdown. The rates of TCE degradation with time were estimated for three catalysts and a blank as a control. As Fig. 2 illustrates, the extent of reaction speedup provided by the catalysts was variable. PTPP led to a marked increase in the Cl⁻ concentration in the aqueous phase during the first 20 to 25 min of the experiment. These results suggest a remarkable enhancement to the rate of TCE degradation. After this early response, the rate of Cl⁻ release with time slowed. Although the greatest enhancement was evident with PTPP, the slopes obtained with two ammonium salts in Fig. 2 also reflect a noticeable increase in TCE destruction as compared to the control experiment. The pattern of reaction speedup, PTPP > TBA > TEA > Blank, is consistent with the extraction constants (K_E) calculated based on the
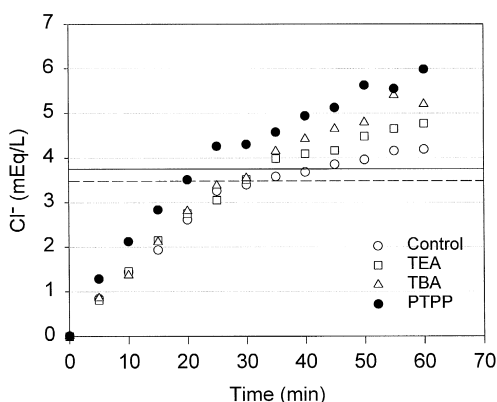

Fig. 2. Concentration of chloride ion released from permanganate oxidation of TCE with different PTCs. Horizontal lines indicate the stoichiometrically expected chloride concentration from complete consumption of MnO_4^- (solid) and the experimentally measured chloride concentration (dotted).

solubilities in the organic phase of methylene chloride (Table 3). In other words, PTPP with the largest extraction constant of the three was the most efficient in transferring MnO_4^- to the TCE phase. These results indicate that PTPP would be the most effective catalyst in speeding up the oxidation of TCE by MnO_4^-.

The noticeable change in reaction rates occurring at 20 to 25 min coincides with a concentration of Cl^- of 3.5 mEq/l (Fig. 2). This Cl^- production represents about 93% of the total Cl^- that would be expected (i.e., 3.75 mEq/l) from the stoichiometry, given an initial permanganate concentration (2.5 mM). Our calculation is based on:

$$C_2Cl_3H + 2MnO_4^- \rightarrow 2CO_2 + 2MnO_2 + 3Cl^- + H^+ \tag{9}$$
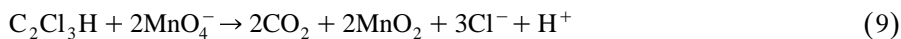
During the early phase of the reaction, MnO_4^- would mainly participate in the oxidation. After the complete consumption of MnO_4^-, less efficient oxidation can be accomplished with MnO_2, causing TCE to breakdown more slowly. The breakpoint in reaction rates probably indicates the transition in oxidants from MnO_4^- to MnO_2.

Although MnO_4^- would form ion pairs with the catalytic cations and be transferred into the nonpolar media, we were not sure whether the catalysts would impact the oxidation of TCE by MnO_2 in the aqueous phase. The catalysts could influence the extent of hydration shell formation around MnO_2 molecules and consequently, the interaction between MnO_2 and dissolved TCE could be affected. Additional work is required to study the behavior of catalysts in solution with the suspended colloidal materials.

4.2. UV–Vis absorbance monitoring

Once catalysts were added to the system, we observed that the color of TCE phase, initially colorless and transparent, changed to a purple color due to the permanganate transfer. The TCE phase became clear once the reaction was completed and the MnO_4^- was used up. The purple color of the TCE phase was most distinct with PTPP. We measured of the concentration of MnO_4^- in the aqueous phase with time using UV–Vis absorbance measurements. Fig. 3 displays UV–Vis spectra successively changing with time for the four different treatments. Decreases in the maximum absorbance at 526 nm indicated the loss of MnO_4^- as it reacted with TCE. The rapid decrease of maximum absorbance with PTPP confirms that PTPP is the most efficient catalyst in transferring MnO_4^- into the TCE phase, and in enhancing the permanganate consumption. This result is consistent with the other observations, such as the rapidly increasing Cl^- concentration observed in the PTPP-catalyzed reaction and the distinct coloration of TCE phase with permanganate transfer.

The UV–Vis spectra showed an isobestic point at 469 nm until the point shifted to a lower wavelength after about 40 min (Fig. 3). This shift in the isobestic point in the spectra was observed earlier with PTPP than with other catalysts. The shift might be caused by the precipitation of MnO_2. Variation in absorbance at 418 nm (Fig. 4) indicates the precipitation of MnO_2 (Mata-Perez and Perez-Benito, 1985). The highest absorbance at 418 nm corresponded to the starting point for MnO_2 precipitation. The subsequent decrease in the magnitude is due to the removal of MnO_2 from the solution
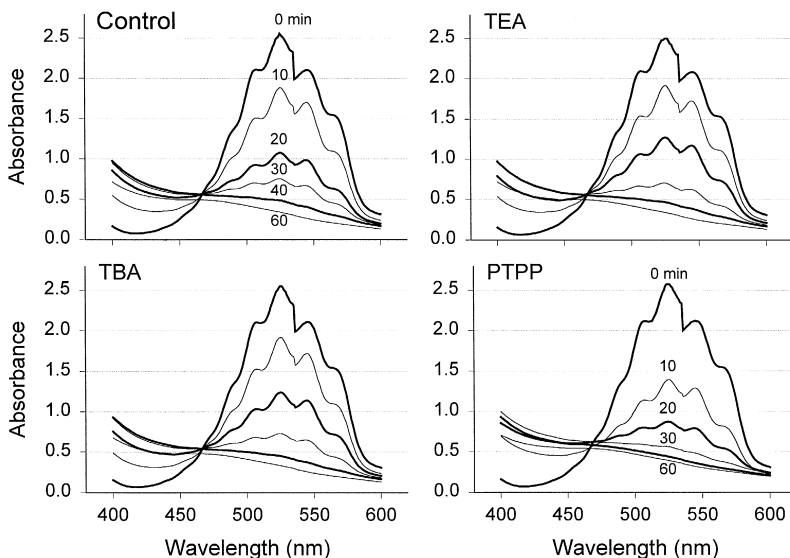
Fig. 3. UV–Vis spectra of aqueous phase in permanganate oxidation of TCE facilitated with different PTCs. Numbers on graphs indicate the reaction time (min).

by precipitation. The time taken to reach the maximum absorbance at 418 nm was about 30 min with PTPP, less than any of the other treatments. The time for conversion of soluble manganese species to MnO_2 was likely reduced due to the rapid permanganate oxidation. The more rapid loss of MnO_4^- and formation of MnO_2 were evidences for accelerated TCE oxidation with PTPP.

The disappearance of MnO_4^- with TCE oxidation can be quantified with UV–Vis absorbance at 526 and 418 nm. Because MnO_4^- is almost transparent at 418 nm and
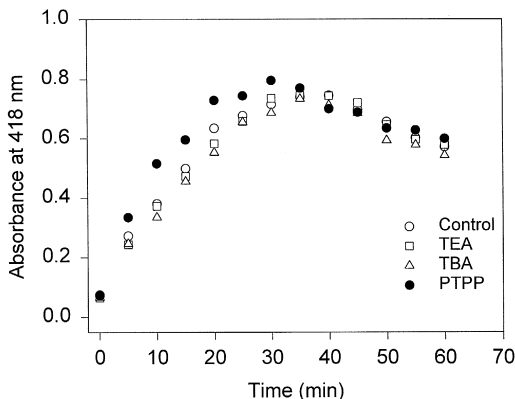

Fig. 4. Variation in the absorbance at 418 nm with time in the aqueous phase as a consequence of TCE oxidation by MnO_4^-, catalyzed with different PTCs.

both species absorb light at 526 nm (Stewart, 1965), the absorbance (A) at 418 and 526 nm can be given as:

$$A_{418} = \varepsilon^{418}_{MnO_2}(c_o - c_t) \tag{10}$$

$$A_{526} = \varepsilon^{526}_{MnO_4^-}c_t + \varepsilon^{526}_{MnO_2}(c_o - c_t) \tag{11}$$

where ε is the molar absorptivity of the manganese species (MnO_2 or MnO_4^-) at the wavelength (418 or 526 nm), c_o is the initial MnO_4^- concentration, c_t is the concentration of MnO_4^- at time t (Freeman and Kappos, 1985; Mata-Perez and Perez-Benito, 1985). From Eqs. (10) and (11), we can deduce an equation for MnO_4^- concentration:

$$\frac{c_t}{c_o} = \frac{A_{526} - \left(\varepsilon^{526}_{MnO_2}/\varepsilon^{418}_{MnO_2}\right)A_{418}}{\varepsilon^{526}_{MnO_4^-}c_o} \tag{12}$$

The denominator on the right side of Eq. (12) is equal to the absorbance of initial permanganate solution at 526 nm. The ratio of molar absorptivity for MnO_2 in the numerator was measured after MnO_4^- had been used up completely. This equation is based on assumptions that there are no other manganese species except MnO_4^- and MnO_2 and that flocculation or precipitation of MnO_2 in the solution is minimal over the time of concern.

The variation in MnO_4^- concentration, expressed as $\log(c_t/c_o)$ with time, is depicted in Fig. 5. As expected, the MnO_4^- concentration was reduced faster with PTPP than with other treatments. The functions were convex, which probably result from the shortage of MnO_4^- available to react with TCE later in the experiment. As MnO_4^- concentration decreases with consumption in the reaction, TCE concentration increases slightly because of the continuous dissolution of pure phase. Because these two parameters vary in the course of the reaction, it cannot be considered strictly as a pseudo-first-order reaction. However, to help compare results, pseudo-first-order rate constants (k) were determined from the slopes of the $\log(c_t/c_o)$ vs. time data in Table 4, using only the
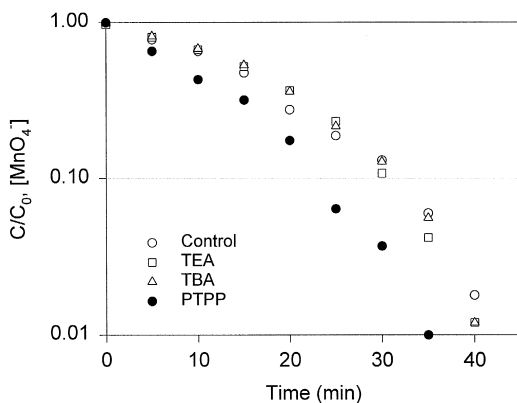

Fig. 5. Relative concentration of MnO_4^- in the aqueous phase as a consequence of TCE oxidation catalyzed with different PTCs.

Table 4
Pseudo-first-order rate constants for permanganate consumption and TCE degradation by oxidation with permanganate

Catalyst	Control	TEA	TBA	PTPP
k (min^{-1})[a]	0.0475	0.0424	0.0408	0.0791
r^2	0.9857	0.9926	0.9962	0.9927
TCE destroyed (mg/min)[b]	0.0169	0.0188	0.0185	0.0248

[a]Calculated from straight portion of relationships between $\log(c_t/c_o)$ and time (15 min).

[b]Calculated with chloride concentration assuming zero-order destruction rate within 15 min in the presence of excessive amount of permanganate.

early straight portion of curves. We calculated stoichiometrically destroyed TCE amounts with chloride concentrations, assuming that MnO_4^- was present in excess in the system and that chloride release is a zero-order reaction within 15 min of reaction time (Table 4). The rate constants and destructed TCE amount verified that the consumption of MnO_4^- and the degradation of TCE were more rapid with PTPP than the other catalysts and potassium permanganate by itself.

4.3. Dissolution of TCE

Quaternary ammonium or phosphonium salts used as PTCs have structural features in common with surfactants employed in remedial systems. The capability of surfactants to solubilize nonpolar organic solutes in the aqueous phase is well-known (Rosen, 1978; Schwartz and Perry, 1978). The problem for our experiments is that the solubilization in the aqueous phase, if it occurred, might enhance rates of TCE destruction. Effectively, enhanced solubility could increase the rate of transfer of TCE into the aqueous phase. Accordingly, we undertook experiments to examine the potential for the solubility enhancement of TCE by PTCs (TBA and PTPP). The experiments involved kinetic batch experiments, looking at TCE increase in the solution with time, as a function of the additives. The results showed no significant difference in TCE concentration for the first 30 min, as compared to trials without PTCs (Fig. 6). Overall, there was a tendency for somewhat reduced solubilities with the PTCs after 24 h of equilibrium.
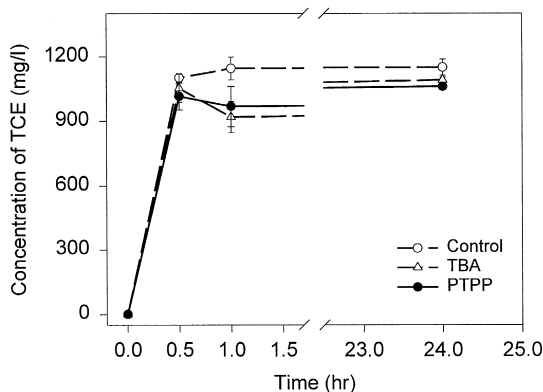

Fig. 6. Variation in the concentration of TCE in the aqueous phase as a function of time and the PTCs.

Commonly, surfactants consist of a long hydrophobic alkyl chain and a large hydrophilic head. PTCs are different in that they are relatively short chains. Because of this structural difference with other surfactants, the formation of pseudo-phase micelles through self-association is minimal even at the high concentration of PTCs. As a result, the solubilization power of PTCs is not comparable to common surfactants, as our experiments show. In addition, below the critical micelle concentration of surfactants, no significant enhancement in the solubility of nonpolar organic solutes is usually observed (Moroi et al., 1983; Kile and Chiou, 1989). Considering the relatively large solubility of TCE in the aqueous phase ($\cong 1100$ mg/l), a small increase in TCE concentration with the addition of small amount of PTC would not measurably increase rates of permanganate oxidation of TCE in the aqueous phase.

Our experiments suggest that there is no enhancement in the rate of TCE decomposition due to solubilization by the PTCs. On the contrary, the concentration of TCE is reduced with the addition of PTCs. This behavior is explainable as a salting-out effect, whereby the solubility of organic compounds would be reduced in high salinity solutions.

5. Conclusions

These preliminary experiments point to significant opportunities for enhancing the oxidation of chlorinated solvents, like TCE, by MnO_4^-. Speed up in oxidation rates was evidenced in our experiments by (1) an increase in the rate of Cl^- production, (2) a more rapid disappearance of MnO_4^- from the aqueous phase, and (3) qualitative changes in the coloration of the TCE phase (clear, to purple, and to clear). Experimental evidence discounted the possibility that the solubilization of TCE in the aqueous phase contributed to the rate enhancement. All of the results confirm that the enhancement in TCE decomposition is due to reactions between MnO_4^- and TCE in the nonaqueous phase, in addition to oxidation of TCE in the aqueous phase.

Of all the catalysts, PTPP was most effective in transferring the reactant into the nonaqueous phase and promoted the greatest increase in the oxidation rate. Theory also provides a useful way to screen potential PTCs for use in remedial applications, for example, the largest extraction constant (K_E), was determined for PTPP, which turned out to be the most efficient catalyst for MnO_4^- transfer.

We think that phase-transfer catalysis has some potential for application in DNAPL remediation. Catalyzed nonaqueous phase reactions could not only increase contaminant degradation rates but also help reduce costs for permanganate recirculation by increasing permanganate participation in the remedial scheme. The catalytic reaction would be most effective for contaminants with an extremely low solubility in the aqueous phase. Such contaminants are often hard to treat in aqueous reaction systems. Extensive studies on the nonaquatic decomposition of the contaminants would be required to explore more efficient PTCs and target contaminants.

In field situations, contaminants can occur as a mixture of various organic compounds in a field situation. A catalytic reaction system could be designed to optimize the

effectiveness of the destruction, when individual compounds are considered separately as organic solvents for catalysts or target solutes for the reactions. Some chlorinated ethylenes such as TCE, *trans*-DCE and 1,1-DCE are very reactive with MnO_4^- but they are poor solvents for quaternary ammonium salts. Some chlorinated ethanes including perchloroethane and trichloethane are not very reactive with MnO_4^- but they are excellent solvents for quaternary ammonium salts. The effectiveness of the catalysis would be maximized in the field when these two groups of compounds are found together. Clearly, additional experimental work is required to study DNAPL mixtures in order to elucidate processes of phase-transfer catalysis in a more realistic situation.

There is a concern that MnO_4^- might be consumed by organic matter in soils and sediments prior to reaching the target contaminant. The same kind of problem could develop with PTCs because they are cationic and may be strongly attracted by cation exchange sites on soil and sediment surfaces. Work is needed to examine the affinity of PTCs for adsorption and whether this process might reduce their effectiveness as catalysts. There are potential work-arounds to this problem. For example, one could pretreat the geological medium to add other cations to exchange sites, or develop an injection technology that delivers the solution directly to the target contaminants.

We are continuing work to develop the catalytic scheme for permanganate oxidation. We are interested in further studying mechanisms of catalytic reaction in nonaqueous phase with various PTCs and the impact of PTC addition on DNAPL mobility and solubility. Evaluation of phase transfer assisted solvent oxidation at larger scales including column or tank experiment is required before any field demonstrations.

Acknowledgements

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